Catalysis Letters 43 (1997) 229–233

Synergy effects in the oxidative dehydrogenation of propane over $MgMoO_4$–MoO_3 catalysts

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Received 24 June 1996; accepted 16 November 1996

Oxidative dehydrogenation of propane was studied over $MgMoO_4$–MoO_3 catalysts with a wt% of MoO_3 varying from 0 to 100. The samples were characterized by XRD, EPR, DTA, laser Raman, and BET. The catalytic behavior of the mechanical mixtures was quite different from that of pure phases. These differences were discussed in terms of possible synergy effects between the phases. Propane conversion and selectivity to propene were closely related to the change in redox properties of the catalysts due to the appearance of Mo^{5+} ions.

Keywords: propane, oxidative dehydrogenation of alkanes, magnesium–molybdenum oxide catalyst characterization (XRD/EPR/DTA/laser Raman)

1. Introduction

In a previous study on the oxidative dehydrogenation of propane it has been found that the Mg–Mo–O system provides a high selectivity to propene with conversion below 6% [1]. An exhaustive characterization allowed us to explain the different catalytic behavior of mixed oxides. The formation of a complex containing Mo^{5+} was assumed to provide the active center for the reaction. At least two phases were simultaneously identified on Mg–Mo–O catalysts. The samples with $MgMoO_4$ and some excess of MoO_3 were the most active ones for selective propane oxidation. The overall catalytic behavior could not be attributed to just one phase. Other catalytic systems have shown a similar behavior in the oxidative dehydrogenation of propane. Thus, Mg orthovanadate can promote selectivity to propene over V–Mg–O catalysts by either a coexisting pyrovanate phase or an excess of MgO in intimate contact [2].

It is well known that phases inactive or poorly active by themselves can modify the catalytic activity of other phases. Activity and/or selectivity enhancement, which has been observed when two phases are present, is of wide interest [3–10]. Various interactions are possible between the components involved in these systems. A fundamental understanding of the physical and chemical nature of these materials and their relation to catalysis is being widely studied. Thus, the present work focuses on the physicochemical characterization of mechanical mixtures containing different amounts of $MgMoO_4$ and MoO_3. In addition, it shows that a synergetic cooperation takes place between the two phases in the oxidative dehydrogenation of propane.

2. Experimental

2.1. Catalyst preparation

Preparation of pure oxides. $MgMoO_4$ was prepared by dissolving $MgCl_2$, ammonia heptamolybdate and citric acid in distilled water. After evaporating of the solvent at 323 K under reduced pressure, the solid obtained was dried at 373 K overnight in a vacuum oven and then calcined at 823 K for 8 h [11]. MoO_3 was prepared from ammonia heptamolybdate following the procedure mentioned above.

Preparation of mechanical mixtures. Mechanical mixtures of separately prepared $MgMoO_4$ and MoO_3 oxides were obtained with different MoO_3 contents. The corresponding powders were dispersed and mixed in *n*-pentane with the help of an ultrasonic device and were subsequently evaporated under reduced pressure to remove the solvent. The solid was dried at 373 K overnight. No further calcination was carried out in the corresponding mechanical mixtures. The samples with 5, 20 and 95 wt% of MoO_3 were named as MM5, MM20 and MM95, respectively.

2.2. Catalyst characterization

Specific surface areas (SA, m^2/g) of mechanical mixtures were determined from krypton adsorption isotherms at 77 K by the BET method. A Micromeritics Accusorb 2100E apparatus was used.

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X-ray diffraction (XRD) patterns were obtained by using a Rigaku diffractometer operated at 35 kV and 30 mA by employing Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm).

Raman spectra were collected with a JASCO TRS600SZP multichannel monochromatic spectrometer. The samples were pressed into self-supporting wafers. The spectra were recorded at room temperature and with a 514.5 nm line excitation radiation of an Ar ion laser. The laser power used was 200 mW.

The EPR measurements were obtained with a Bruker spectrometer operated at X-band frequencies at room temperature and a Klystron frequency of 9.7 GHz and 100 kHz magnetic field modulation. The spectrometer was equipped with an on-line computer for data treatment.

DTA measurements were performed by a DTA 50 Shimadzu apparatus from room temperature to 1073 K in N_2 and air flow (60 and 40 ml/min, respectively), using α-Al_2O_3 as reference and a temperature rise rate of 10 K/min. For each experiment 20 mg of the sample was used. The sample and the reference of comparable volumes were placed in platinum containers.

2.3. Catalytic test

The catalysts (700 mg, 0.5–0.85 mm particle diameter) were tested in a fixed-bed, quartz tubular reactor operated at atmospheric pressure. The temperature, measured with a coaxial thermocouple, varied between 723 and 823 K. The feed was a mixture of 4 vol% propane, 4 vol% oxygen and balanced with helium. The flow rate was 100 ml/min at room temperature. The reactants and reaction products were alternately analyzed on-line by a Shimadzu GC9A gas chromatograph equipped with a thermal conductivity detector. A Porapaq Q (80–100 mesh) column for separating hydrocarbons and CO_2 and a 2 m activated carbon (30–50 mesh) column for carbon monoxide, methane and oxygen were used. The homogeneous contribution was tested in the empty reactor. These runs showed no activity below 853 K. The results were very similar with and without the use of quartz particles.The conversion and selectivity for products were evaluated for the exit stream [1].

Table 1
Specific surface areas of the catalyts

	$MgMoO_4$	MoO_3	MM5	MM20	MM95
SA_{BET} exp. (m^2/g)	4.64	0.87	5.28	4.1	1.1
SA_{BET} theor. (m^2/g)	–	–	4.50	4.0	1.0

3. Results

Specific surface areas. Table 1 shows the specific surface areas (SA) of the fresh mechanical mixtures. The values are in the range of 5.3 to 1.1 m^2/g which corresponds to the properly averaged sum of those previously measured for the pure oxides. The SA does not change after reaction.

X-ray diffraction. Fig. 1 illustrates the XRD spectra of the MM5, MM20, and MM95 samples. The spectra for fresh MM5 and MM20 catalysts were formed with the strong reflection lines of two phases: monoclinic $MgMoO_4$ and orthorhombic MoO_3. The principal spectrum feature in fig. 1c corresponds exclusively to the con-

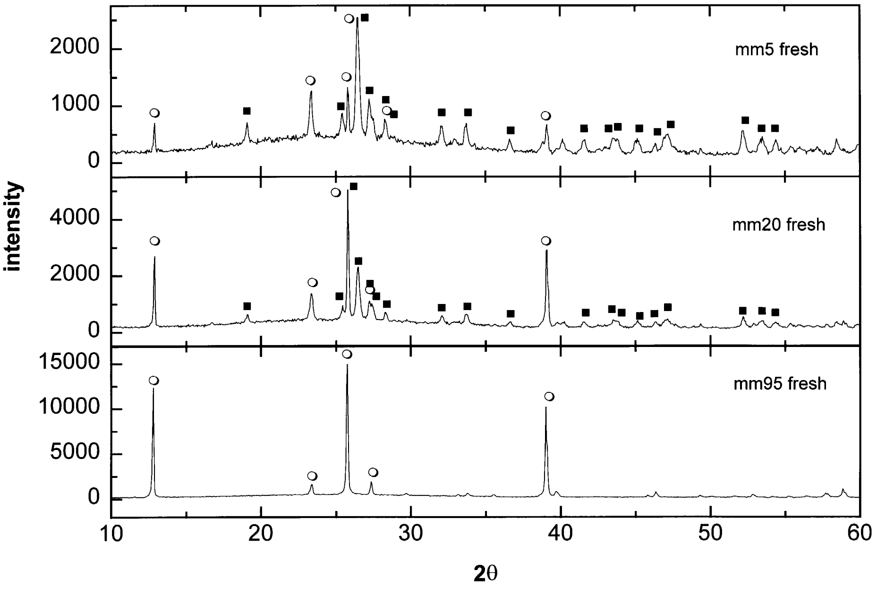

Fig. 1. X-ray patterns of (a) MM5 (5% MoO_3 in $MgMoO_4$), (b) MM20 (20% MoO_3), (c) MM95 (95% MoO_3). (■) Monoclinic $MgMoO_4$ and (○) orthorhombic MoO_3.

tribution of orthorhombic MoO_3. No pattern corresponding to new phases was observed after reaction.

Raman spectroscopy. The Raman spectra of the fresh and the used MM5 sample are shown in fig. 2. The Raman bands at 966, 955, 908, and 852 cm^{-1} were ascribed to magnesium molybdate. The bands at 993, 815, and 661 cm^{-1} were assigned to MoO_3. The comparison of the spectra indicates a degree of reduction as evidenced by the intensity loss of MoO_3 bands. Ozkan et al. [5] found the same behavior on the $MnMoO_4$–MoO_3 system when it was reduced at 723 K. Reduction of the samples was also shown by a color change from white to pale gray.

Differential thermal analysis. The DTA analyses made on the samples and the reference oxides showed that no phase transition takes place at temperatures up to 873 K. The results are shown in fig. 3. At a temperature exceeding 873 K, an exothermic effect was found in MoO_3 due to sublimation. After the DTA analysis a mass decrease was also observed. These results from the sublimation of molybdenum trioxide were not found in mechanical mixtures. Similar results were reported by Oganowski et al. [12], who suggested that MoO_3 is strongly bound to the $MgMoO_4$ and that it begins to sublime at a considerably higher temperature than pure MoO_3.

EPR spectroscopy. EPR measurements were carried out to examine the presence of Mo^{5+}. Spectra of pure samples of MoO_3 and $MgMoO_4$ recorded at room temperature revealed no significant presence of Mo^{5+} ions even after reaction. The presence of these species was not detected in all mechanical mixtures before being used, either. However, spectra of MM5 and MM20 after the oxidative dehydrogenation of propane showed a similar signal characteristic of Mo^{5+}. The EPR spectra are shown in fig. 4. The average g value was 1.926, which was assigned to Mo^{5+} [1,12]. The line for MM5 was more intense than the line for MM20. No signal was observed for MM95.

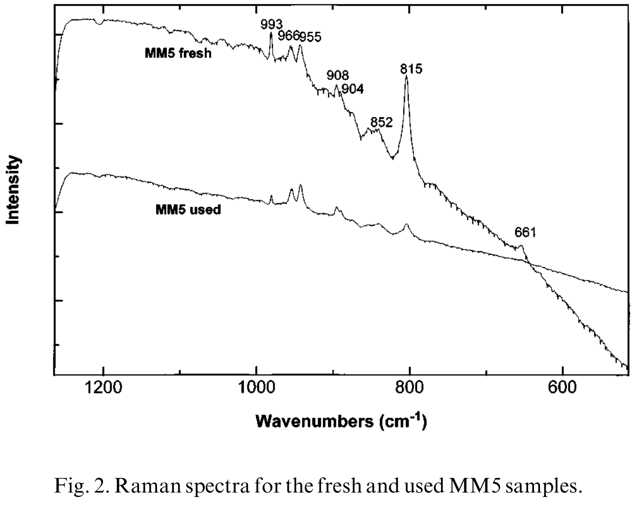

Fig. 2. Raman spectra for the fresh and used MM5 samples.

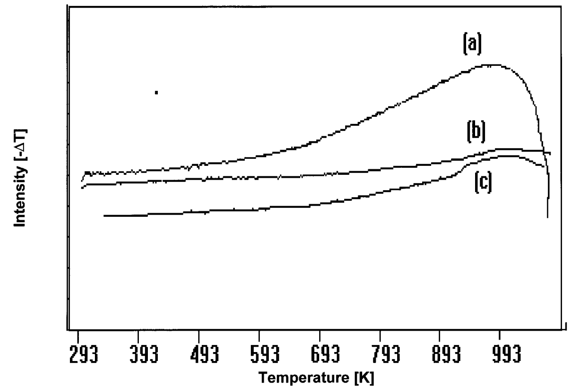

Fig. 3. DTA diagrams for MoO_3, MM5 and MM20 catalysts.

Catalytic results. Table 2 summarizes the catalytic results for MM5 and MM20 catalysts in the oxidative dehydrogenation of propane. Both pure phases and the MM95 sample were inactive. MoO_3 exhibited a very low conversion (0.56%) at 823 K. Propene and CO_2 were the main products in the temperature range between 723 and 823 K. Ethene was only produced at 823 K. Oxygenated products other than carbon dioxide were not detected and no deactivation by coke formation was observed. The selectivity to propene was higher than 90% and it decreased when propane conversion increased. As shown in table 2, the MM5 catalyst was the most active and its yield of propene was also the highest. In fig. 5 the propene yield is plotted as a function of the propane conversion for MM5 and MM20 samples. It is observed that all points fit the same curve. Then, it can be assumed that the same type of active site is present at the surface of both catalysts which would differ only in the superficial site concentration.

Catalytic experiments were carried out for 7 h. No deactivation was observed.

4. Discussion

Mechanical mixtures of $MgMoO_4$ and MoO_3 show a significant synergy effect in the oxidative dehydrogenation of propane. $MgMoO_4$ in close contact with MoO_3 is much more active and selective than the pure phases. To explain the synergy observed, the results of the catalyst characterization are examined.

(i) No changes in surface areas take place and the texture of the pure oxides is not modified when they form the mechanical mixtures.

(ii) X-ray diffraction patterns show that the samples remained intact after being exposed to reaction conditions for 7 h. No new phases were observed. DTA measurements show also no phase transition in the temperature range used in this work. Raman spectroscopy only reveals a certain reduction after reaction, as

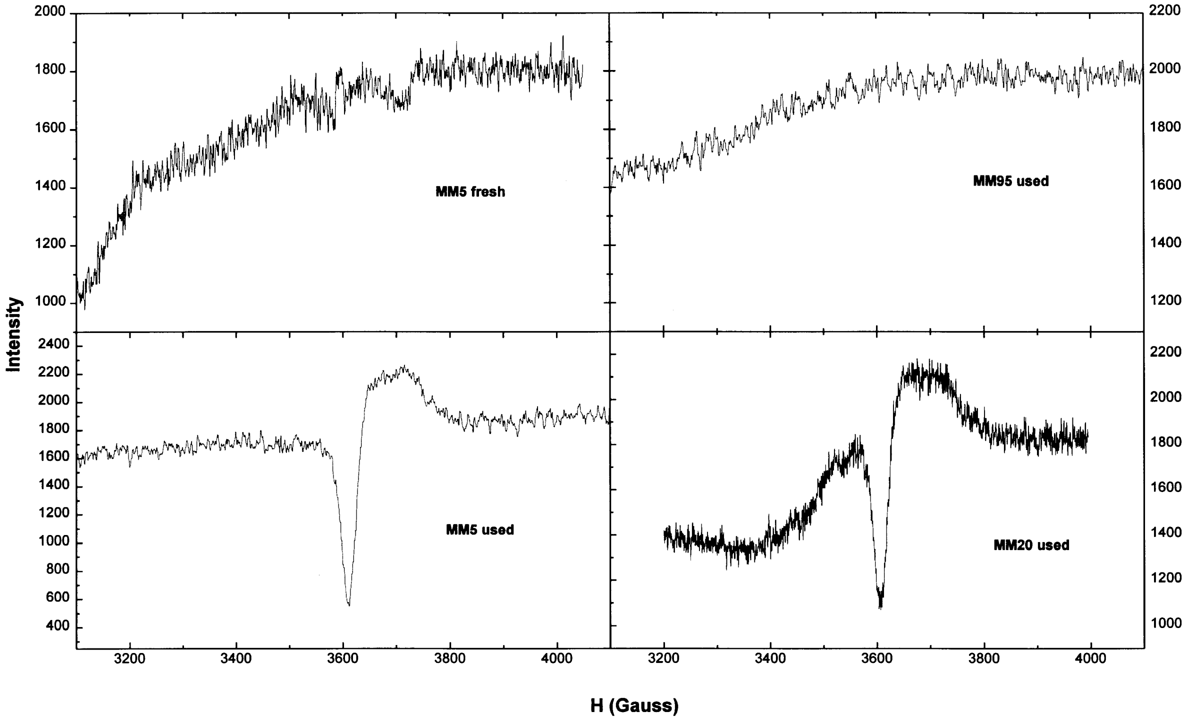

Fig. 4. EPR spectra for (a) fresh MM5, (b) used MM5, (c) used MM20, (d) used MM95.

evidenced by the intensity loss of the Raman bands of MoO_3 (fig. 3).

(iii) Since the synergy could also be attributed to a contamination by Mo volatilization and condensation, a sample artificially contaminated and obtained by impregnation has also been studied. 5% of molybdenum from an ammonia heptamolybdate solution was impregnated over $MgMoO_4$, dried and calcined at 823 K for 5 h. In the temperature range studied, the conversion and yield to propene on the impregnated sample were lower than the values for the MM5 sample. During the impregnation, Mo is put in intimate contact with Mg, allowing a solid state reaction to occur in the calcination step. In fact, the XRD pattern for the fresh sample revealed the formation of the polymolybdate phase, $Mg_2Mo_3O_{11}$. In an early work about the oxidative dehydrogenation of propane over MgMoO catalysts, Cadus et al. [1] reported that the polymolybdate phase was inactive. Its presence could explain the lower conversion and the yield of propene obtained over the impregnated sample. The catalytic results are also plotted in fig. 5. The points fit the same curve, indicating that the same type of active sites present in mechanical mixtures are involved. If the tendency of the mechanical mixtures was the contamination of $MgMoO_4$ by molybdenum, a solid state reaction

Table 2
Catalytic results for propane oxidation over $MgMoO_4/MoO_3$ mechanical mixtures. Propane : $O_2 = 1 : 1$; catalyst weight = 700 mg; $W/F = 185$ g min mol^{-1}. X (%), conversion of propane; S_i (%), selectivity to product i

T (K)	MM5			MM20		
	723	773	823	723	773	823
X (%)	1.62	4.45	9.50	0.0	2.54	7.14
$S_{C_3^=}$ (%)	97.6	95.2	90.8	0.0	98.4	93.7
S_{CO_2} (%)	2.4	4.8	7.4	0.0	1.6	6.2
S_{C_2} (%)	0.0	0.0	1.8	0.0	0.0	traces

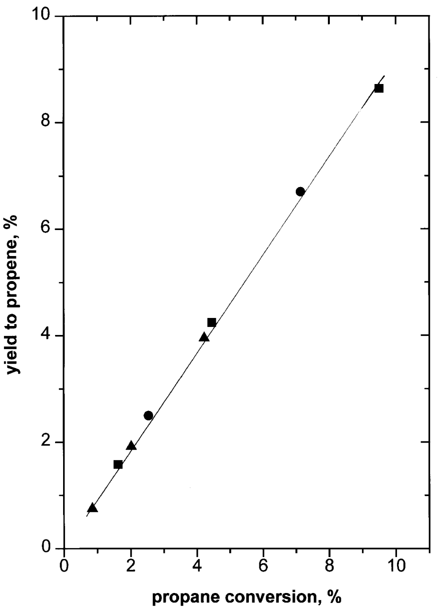

Fig. 5. Propene yield as a function of propane conversion over $MgMoO_4$–MoO_3 mechanical mixtures. (■) MM5, (●) MM20, (▲) Mo^{6+} impregnated on $MgMoO_4$.

should occur leading to a less active catalyst which opposes our results.

(iv) Another explanation for the synergy observed could be a phase cooperation, allowing MoO_3 crystallites to be oriented on the surface of $MgMoO_4$ and thereby create catalytically active sites not found in the isolated phases. The structures of MoO_3 (orthorhombic Pnma) and of $MgMoO_4$ (monoclinic C2/m) could show a crystallographic fit similar to the strong isomorphism found between MoO_3 and $CoMoO_4$ due to the fact that the structure of both molybdates is the same. The crystallographic fit between MoO_3 and $CoMoO_4$ structures of edge-sharing octahedra is possible along the axis. Distances Mo–Mo of MoO_3 and Mo–Co of $CoMoO_4$ are quite compatible [13]. But it is difficult to accept that a very simple mixture of two powders prepared separately allows a "very precise" matching of two "very precise" faces in an amount that explains the activity increase [8].

(v) Changes in the oxidation state of molybdenum are observed in all mechanical mixtures after being used. EPR measurements show a signal characteristic of Mo^{5+}.

The signal of Mo^{5+} is also present on the fresh and the used impregnated sample. The presence of Mo^{5+} ions on the fresh catalyst could be attributed to the calcination process [12]. The intensity was higher in the used sample suggesting that propane contributes to surface reduction.

From EPR measurements and the catalytic experiments, it can be observed that the MM5 sample with the highest Mo^{5+} signal leads to the highest propane conversion and propene yield. Therefore, it is possible to consider that this reduced form of molybdenum is involved in the reaction and the activation of the catalyst takes place under the propane atmosphere. Khan and Somorjai [14] proposed that the active sites on the molybdenum-based catalyst for methane oxidation are pairs of coupled Mo^{5+} and Mo^{6+} species undergoing a redox cycle mechanism. Ward et al. [15] also suggested that the active sites in MoO_3/SiO_2 for the oxidative dehydrogenation of ethane are an active form of Mo^{5+}.

The evidence obtained indicates that $MgMoO_4$–MoO_3 catalyst shows the existence of a synergy effect in the oxidative dehydrogenation of propane. Similar effects were previously observed over other molybdate–molybdenum oxide catalytic systems [4–7]. From the above discussion it can be suggested that the C–H bond cleavage of propane takes place on the surface of the catalyst having well-defined redox properties. It is clear that some physicochemical modifications occur during reaction which could explain synergy effects. The characterization techniques have shown that the mechanical mixtures are always composed by two phases. No new phases are formed. No decomposition or contamination of the phases is observed after reaction. But some modifications of the redox properties are put in evidence by EPR measurements. Propane conversion and selectivity to propene are closely related to the change in redox properties of the catalysts due to the appearance of Mo^{5+} ions.

The changes in the catalyst activity might be accounted for by the creation of new active sites. The exact reason for the creation of these sites is not within the scope of this work, although it is a subject of study in the current research.

The selectivity of propene obtained (91%) at ca. 10% conversion of propane shows that the $MgMoO_4$–MoO_3 system could be quite a promising catalyst for the oxidative dehydrogenation of propane.

Acknowledgement

The authors are grateful to Japon International Cooperation Agency for granting the Laser Raman Spectrometer to CENACA. Financial support is acknowledged to CONICET and to Universidad Nacional de San Luis as well.

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